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FEC 165NP

SUBSTITUTE SPECIFICATION

QUINONE-BASED COMPOUND, AND ELECTROPHOTOGRAPHIC

PHOTORECEPTOR AND ELECTROPHOTOGRAPHIC APPARATUS USING THE

SAME

TECHNICAL FIELD

[0001]

The present invention relates to a quinone-based compound and in detail, it relates to a novel quinone-based compound which is useful as an electron transport substance in an electrophotographic photoreceptor (hereinafter also referred to simply as "photoreceptor"), an organic electroluminescence or electroluminescent (EL) device, and the like. Also, the invention relates to an electrophotographic photoreceptor and an electrophotographic apparatus and in detail, it relates to an electrophotographic photoreceptor using a specific compound as an electron transport substance and to an electrophotographic apparatus using this electrophotographic photoreceptor.

BACKGROUND ART

[0002]

In recent years, a number of organic photoreceptors using an organic photoconductive material have been proposed and put into practical use as one of electronic devices using an organic compound from the viewpoint that it is possible to design photoreceptor characteristics that can be manufactured without pollution, at low

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cost, and with flexibility in choosing materials or design characteristics.

[0003]

A photosensitive layer of an organic photoreceptor is comprised of a layer in which an organic photoconductive material is mainly dispersed in a resin. There have been made a number of proposals including a layered type structure in which a layer having a charge generation substance dispersed in a resin (charge generation layer) and a layer having a charge transport substance dispersed in a resin (charge transport layer) are laminated. Another proposal is a single layer type structure comprising a single layer having both a charge generation substance and a charge transport substance dispersed in a resin.

[0004]

Above all, a photoreceptor with functionally separated layers includes, as a photosensitive layer, a charge generation layer having a charge transport layer thereon is widely put into practical use because it has excellent photoreceptor characteristics and durability. In the charge transport layer provided in this functionally separated layered photoreceptor, in general, a hole transport substance is used as a charge transport substance. Therefore, this photoreceptor is used in an electrophotographic apparatus which is actuated in a negative charge process. However, since a corona discharge with negative polarity to be used in the negative charge process is unstable as compared with that with positive polarity and generates a high amount of ozone, the photoreceptor is prone to physical and chemical deterioration and to create an adverse effect upon the environment. In order to solve these problems, an organic photoreceptor which can be used in the positive charge process is effective.

[0005]

Now, in order to make the photoreceptor having excellent durability as described previously useful in the positive charge process and having high sensitivity, it is necessary to use a substance having an excellent electron transport function. To date, a number of proposals have been made with respect to such a substance and a photoreceptor using the same. For example, in Patent Documents 1 to 14, Non-Patent Documents 1 to 4 and others, a number of electron transport substances and electrophotographic photoreceptors using the same are proposed and described, and have received attention. Furthermore, for example, as described in Patent Documents 15 to 19 and others, photoreceptors using a combination of a hole transport substance and an electron transport substance in a single layer type photosensitive layer have received attention for the reason that they have high sensitivity, and some have been put into practical use.

[0006]

Furthermore, the present inventors have proposed a variety of photoreceptors containing a substance having an electron transport function for the purpose of realizing a photoreceptor having improved characteristics (for example, as described in Patent Documents 20 to 24 and so on).

[0007]

Moreover, in recent years, an organic EL light emitting device using an organic photoconductive substance is known, which is expected to be applied to a display.

With respect to this organic EL device, a number of proposals regarding improvements of an organic material have also been made, and have been put into practical use.

[8000]

The simplest structure of the organic EL device is a structure in which a light emitting layer containing a light emitting material which is an organic compound is interposed by electrodes. By making a current flow into the electrodes, an electron and a hole are injected from the electrodes into the light emitting layer, an exciton is formed in the light emitting layer, and recombination takes place, thereby generating light emission.

Furthermore, for the purpose of effectively injecting an electron and a hole from the electrodes into a light emitting layer or other purposes, a structure in which functional layers such as a hole transport layer, a hole injection layer, an electron transport layer, and an electron injection layer are laminated together with a light emitting layer is also proposed. Among these layers, an organic compound having an electron transport function is used in the electron transport layer and the electron injection layer (see, for example, Non-Patent Document 5).

The documents referenced above are as follows:

Patent Document 1: JP-A-1-206349

Patent Document 2: JP-A-4-360148

Patent Document 3: JP-A-3-290666

Patent Document 4: JP-A-5-92936

Patent Document 5: JP-A-9-151157

Patent Document 6: JP-A-5-279582

Patent Document 7: JP-A-7-179775

Patent Document 8: JP-A-10-73937

Patent Document 9: JP-A-4-338760

Patent Document 10: JP-A-1-230054

Patent Document 11: JP-A-8-278643

Patent Document 12: JP-A-9-190002

Patent Document 13: JP-A-9-190003

Patent Document 14: JP-A-2001-222122

Patent Document 15: JP-A-5-150481

Patent Document 16: JP-A-6-130688

Patent Document 17: JP-A-9-281728

Patent Document 18: JP-A-9-281729

Patent Document 19: JP-A-10-239874

Patent Document 20: JP-A-2000-75520

Patent Document 21: JP-A-2000-199979

Patent Document 22: JP-A-2000-143607

Patent Document 23: JP-A-2001-142239

Patent Document 24: JP-A-2002-278112

Non-Patent Document 1: *The Journal of Imaging Society of Japan*, Vol. 30, pp.266-273 (1991)

Non-Patent Document 2: Preprint of Pan-Pacific Imaging Conference/Japan Hardcopy '98, July 15-17, 1998, JA HALL, Tokyo, Japan, pp.207-210

Non-Patent Document 3: *Collected Papers of Japan Hardcopy '97*, July 9, 10 and 11, 1997, JA HALL (Otemachi, Tokyo), pp.21-24

Non-Patent Document 4: Collected Papers of Japan Hardcopy '92, July 6, 7 and

8, 1992, JA HALL (Otemachi, Tokyo), pp.173-176

Non-Patent Document 5: *OYO BUTURI*, Vol. 70, No. 12 (2001), pp.1419-1425, "Recent development of highly efficient organic EL materials (by Ohmori)"

[0009]

However, diphenoquinone compounds and stilbenequinone compounds, which are known as substances having an electron transport function, cannot sufficiently satisfy the necessary electrical characteristics such as sensitivity and residual potential required for use in an electrophotographic photoreceptor. For that reason, an electron transport substance having better electrical characteristics has been desired. In addition, it has been desired to realize an electrophotographic photoreceptor and an electrophotographic apparatus that have higher performance by using such an electron transport substance. Also, in the applications of an organic EL device, an electron transport substance with high performance, which has a luminance higher than that of conventional electron transport substances and which can enhance luminous efficiency, has been demanded.

[0010]

OBJECTS AND SUMMARY OF THE INVENTION

Then, an object of the invention is to provide a compound having an excellent electron transport function, which is useful for an electrophotographic photoreceptor and applications of an organic EL device. Another object of the invention is to provide an electrophotographic photoreceptor including an electrically conductive substrate having

thereon a photosensitive layer, which has excellent electrical characteristics and is stable in repeated use, by using a compound having excellent electron transport ability. Also an object of the invention is to provide an electrophotographic apparatus using this electrophotographic photoreceptor.

[0011]

In order to solve the foregoing problems and satisfy the objects of the invention, a quinone-based compound of the invention is characterized by having a structure represented by the following general formula (I):

$$\begin{array}{c}
R^{1} \\
R^{2}
\end{array}$$

$$\begin{array}{c}
N = N - R^{5} \\
X \\
(R^{6})_{n}
\end{array}$$
(I)

(in the formula (I), R¹, R², R³, and R⁴ may be the same or different and each represents a hydrogen atom, an optionally substituted alkyl group having from 1 to 12 carbon atoms, an optionally substituted aryl group, or an optionally substituted heterocyclic group; R⁵ represents an optionally substituted aryl group or an optionally substituted heterocyclic group; R⁶ represents a halogen atom, an optionally substituted alkyl group having from 1 to 6 carbon atoms, an optionally substituted alkoxy group having from 1 to 6 carbon atoms, an optionally substituted aryl group, or an optionally substituted heterocyclic group; X represents a sulfur atom or an oxygen atom; n represents an integer of from 0 to 3; when n is 2 or 3, at least two R⁶s may be the same or different and may be taken together to form optionally—a substituted ring or fused ring; and the

substituents each represents a halogen atom, an alkyl group having from 1 to 6 carbon atoms, an alkoxy group having from 1 to 6 carbon atoms, a halogenated alkyl group having from 1 to 6 carbon atoms, a nitro group, an aryl group, or a heterocyclic group.)

[0012]

Furthermore, in order to solve the foregoing problem and satisfy the objects of the invention, an electrophotographic photoreceptor of the invention is an electrophotographic photoreceptor including an electrically conductive substrate having thereon directly or via an undercoat layer a photosensitive layer, which is characterized in that the photosensitive layer contains at least one kind of a compound having a structure represented by the following general formula (I):

(in the formula (I), R¹, R², R³, and R⁴ may be the same or different and each represents a hydrogen atom, an optionally substituted alkyl group having from 1 to 12 carbon atoms, an optionally substituted aryl group, or an optionally substituted heterocyclic group; R⁵ represents an optionally substituted aryl group or an optionally substituted heterocyclic group; R⁶ represents a halogen atom, an optionally substituted alkyl group having from 1 to 6 carbon atoms, an optionally substituted alkoxy group having from 1 to 6 carbon atoms, an optionally substituted aryl group, or an optionally substituted heterocyclic group; X represents a sulfur atom or an oxygen atom; n represents an integer of from 0 to 3; when n is 2 or 3, at least two R⁶s may be the same or different

and may be taken together to form an optionally substituted ring or fused ring; and the substituents each represents a halogen atom, an alkyl group having from 1 to 6 carbon atoms, an alkoxy group having from 1 to 6 carbon atoms, a halogenated alkyl group having from 1 to 6 carbon atoms, a nitro group, an aryl group, or a heterocyclic group.)

[0013]

In the photoreceptor of the invention, it is suitable that the foregoing photosensitive layer is a single layer type photosensitive layer containing a charge generation substance, a charge transport substance, and a resin binder; that an electron transport substance and a hole transport substance are contained as the charge transport substance; and that at least one compound having a structure represented by the foregoing general formula (I) is contained as the electron transport substance. In particular, the photoreceptor of the invention can be suitably applied to an electrophotographic apparatus for performing a charge process by a positive charge process.

[0014]

Furthermore, in the photoreceptor of the invention, heretofore known hole transport substances as described in, for example, JP-A-2000-314969 can be used as the hole transport substance in the photosensitive layer, and it is especially preferred to contain a styryl compound.

[0015]

In addition, in the photoreceptor of the invention, heretofore known charge generation substances can be used as the charge generation substance in the photosensitive layer, and it is especially preferred to contain a phthalocyanine

compound therein. As the phthalocyanine compound, for example, X-type metal-free phthalocyanine, α -type titanyl phthalocyanine, and Y-type titanyl phthalocyanine as described, for example, in JP-A-2001-228637, titanyl phthalocyanine according to the invention as described in, for example, JP-A-2001-330972 and the like are more suitable. However, it should not be construed that the invention is limited thereto.

[0016]

Moreover, an electrophotographic apparatus of the invention is characterized by being provided with the foregoing electrophotographic photoreceptor of the invention and performing a charge process by a positive charge process.

[0017]

According to the invention, it is possible to obtain a compound having excellent electron transport properties, and by applying this compound in an electrophotographic photoreceptor and an electronic device using an organic compound such as an organic EL compound, it is possible to enhance characteristics such as electrical characteristics and luminous efficiency.

[0018]

Furthermore, according to the invention, in the electrophotographic photoreceptor including an electrically conductive substrate having thereon a photosensitive layer, by containing a specific compound having electron transport properties as represented by the foregoing general formula (I) as an electron transport substance in the photosensitive layer, not only the electron transport properties are enhanced and excellent electrical characteristics are exhibited, but also since the

amount of charge trapped becomes a small, an excellent effect in long-term stability is brought about. Consequently, according to the invention, it is possible to obtain an electrophotographic photoreceptor with high durability, which is excellent in electrical characteristics and long-term stability. This electrophotographic photoreceptor is useful for electrophotographic apparatus employing the electrophotographic system such as printers, copiers and facsimile machines.

BRIEF DESCRIPTION OF THE DRAWINGS

- Fig. 1 is a schematic cross-sectional view to show a general construction of an electrophotographic photoreceptor.
- Fig. 2 is a schematic cross-sectional view to show one construction example of a single layer type electrophotographic photoreceptor.
- Fig. 3 is a schematic cross-sectional view to show another construction example of a single layer type electrophotographic photoreceptor.
- Fig. 4 is a schematic cross-sectional view to show one construction example of a layered type electrophotographic photoreceptor.
- Fig. 5 is a schematic cross-sectional view to show another construction example of a layered type electrophotographic photoreceptor.
- Fig. 6 is a schematic cross-sectional view to show a still another construction example of a layered type electrophotographic photoreceptor.
- Fig. 7 is an IR spectrum of a compound represented by the structural formula (I-3).
 - Fig. 8 is a ¹H-NMR spectrum of a compound represented by the structural

formula (I-3).

Fig. 9 is an IR spectrum of a compound represented by the structural formula (I-83).

Fig. 10 is a ¹H-NMR spectrum of a compound represented by the structural formula (I-83).

Fig. 11 is an IR spectrum of a compound represented by the structural formula (I-163).

Fig. 12 is a ¹H-NMR spectrum of a compound represented by the structural formula (I-163).

Fig. 13 is an IR spectrum of a compound represented by the structural formula (I-217).

Fig. 14 is a ¹H-NMR spectrum of a compound represented by the structural formula (I-217).

Fig. 15 is an IR spectrum of a compound represented by the structural formula (I-243).

Fig. 16 is a ¹H-NMR spectrum of a compound represented by the structural formula (I-243).

Fig. 17 is an IR spectrum of a compound represented by the structural formula (I-403).

Fig. 18 is a ¹H-NMR spectrum of a compound represented by the structural formula (I-403).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019]

Specific embodiments of the invention will be hereunder described in detail.

First of all, a quinone-based compound of the invention will be described. The quinone-based compound of the invention as represented by the foregoing general formula (I) can be, for example, synthesized according to the following reaction schemes (1) and (2). That is, as shown in the following reaction scheme (1), a compound represented by the structural formula (B) is first synthesized from a compound represented by the structural formula (B'). Next, as shown in the following reaction scheme (2), this compound represented by the structural formula (B) is allowed to react with a compound represented by the structural formula (A) and an appropriate organometallic reagent (for example, magnesium), and thereafter, a protective group (TMS: trimethylsilyl group) is eliminated to synthesize a compound represented by the structural formula (C). In addition, this compound is subjected to dehydration condensation with a compound represented by the structural formula (D), followed by oxidation with an appropriate catalyst (for example, lead dioxide (PbO₂)). Thus, the compound represented by the structural formula (I) can be synthesized.

Incidentally, the term "TBAF" in the following reaction scheme (2) means tetrabutylammonium fluoride.

Reaction scheme (1)

$$CI \xrightarrow{(R^6)_n} CH_3 ONH CH_3 Pyridine Pyridine Pyridine Pyridine (R^6)_n (R^6$$

Reaction scheme (2)

TMSO
$$\stackrel{R^1}{\longrightarrow}$$
 $\stackrel{R^3}{\longrightarrow}$ $\stackrel{i)}{\longrightarrow}$ $\stackrel{Mg}{\longrightarrow}$ $\stackrel{ii)}{\longrightarrow}$ $\stackrel{CH_3}{\longrightarrow}$ $\stackrel{(R^6)_h}{\longrightarrow}$ $\stackrel{R^2}{\longrightarrow}$ $\stackrel{R^4}{\longrightarrow}$ $\stackrel{R^3}{\longrightarrow}$ $\stackrel{R^4}{\longrightarrow}$ $\stackrel{R^4}{\longrightarrow$

[0020]

Specific examples of the compounds represented by the foregoing general formula (I) will be given below, but it should not be construed that the invention is limited to these compounds. Incidentally, the symbol

+

in the following specific examples means a substituent t-butyl group.

[0021]

[0022]

$$O \longrightarrow F F F \qquad (I-17) \qquad O \longrightarrow F F F \qquad (I-18)$$

$$O \longrightarrow F F \qquad (I-19)$$

$$O \longrightarrow F \qquad F \qquad (I-10)$$

$$0 \longrightarrow N = N \longrightarrow NO_2$$

$$(I-25)$$

$$0 \longrightarrow N = N \longrightarrow NO_2$$

$$(I-26)$$

$$O_{2}N$$

$$N=N-V-CF_{3}$$

$$O_{2}N$$

$$S$$

$$(I-27)$$

$$O_{2}N$$

$$S$$

$$(I-28)$$

$$0 \longrightarrow N = N \longrightarrow (I-29)$$

$$0 \longrightarrow N = N \longrightarrow (I-30)$$

$$(I-30)$$

$$0 \longrightarrow N = N - N \qquad (I-31) \qquad 0 \longrightarrow N = N - N \qquad (I-32)$$

[0023]

[0024]

[0025]

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[0048]

[0049]

[0050]

Since the quinone-based compound of the invention as represented by the foregoing general formula (I) has excellent electron transport properties, it is useful as a so-called electron transport substance. In particular, it can be suitably used as a material for a photosensitive layer of an electrophotographic photoreceptor and a material for a functional layer such as an electron transport layer of an organic EL device.

[0051]

Next, specific embodiments of the electrophotographic photoreceptor of the invention will be hereunder described in detail with reference to the accompanying drawings.

Fig. 1 is a conceptual cross-sectional view to show one embodiment of the photoreceptor of the invention. Reference numeral 1 designates an electrically conductive substrate; reference numeral 2 designates an undercoat layer; reference numeral 3 designates a photosensitive layer; and reference numeral 4 designates a protective layer, respectively, in which the undercoat layer 2 and the protective layer 4 are provided as the need arises. The photosensitive layer 3 includes a single layer type comprising a single layer having both a charge generation function and a charge transport function and a functionally separated type in which separate charge generation and charge transport layers are laminated. Primary specific examples include photoreceptors having a layer construction as shown in Figs. 2 to 6. Figs. 2 and 3 each show a single layer type photoreceptor in which the photosensitive layer 3 is

of a single layer type. Furthermore, Figs. 4 and 5 each show a functionally separated layered photoreceptor in which the photosensitive layer 3 is formed by laminating a charge generation layer 3a and a charge transport layer 3b in this order on the undercoat layer 2. In addition, Fig. 6 shows a functionally separated layered photoreceptor in which the photosensitive layer 3 is formed by laminating a charge transport layer 3b and a charge generation layer 3a in this order and the protective layer 4 is further provided thereon. However, it should not be construed that the invention is limited to the photoreceptors having a layer structure as illustrated in these drawings.

[0052]

The electrically conductive substrate 1 serves as an electrode of the photoreceptor and simultaneously functions as a support for other respective layers, and may be in any of a cylindrical, plate-like or film-like form. With respect to the quality of the material, metals such as aluminum, stainless steel, and nickel; and glass or resin which has been subjected to an electrically conductive treatment, and the like can be employed.

[0053]

The undercoat layer 2 can be provided depending upon the situation and is comprised of a layer containing a resin as the major component or an oxidized film made of alumite or the like. For the purpose of preventing injection of an unnecessary charge from the electrically conductive substrate into the photosensitive layer, or enhancing covering of a defect on the substrate surface or adhesion of the photosensitive layer or the like, the undercoat layer 2 can be provided depending upon the situation. As a resin binder for the undercoat layer, polycarbonate resins, polyester

resins, polyvinyl acetal resins, polyvinyl butyral resins, vinyl chloride resins, vinyl acetate resins, polyethylene, polypropylene, polystyrene, acrylic resins, polyurethane resins, epoxy resins, melamine resins, phenol resins, silicone resins, polyamide resins, polystyrene resins, polyacetal resins, polyallylate resins, polysulfone resins, polymers or copolymers of methacrylic esters, and the like can be properly combined and used. Furthermore, the resin binder may contain one or more kinds of fine particles of metal oxides such as silicon oxide (silica), titanium oxide, zinc oxide, calcium oxide, aluminum oxide (alumina), and zirconium oxide; metal sulfides such as barium sulfide and calcium sulfide; metal nitrides such as silicon nitride and aluminum nitride; and the like. The surface of such fine particles may be subjected to a surface treatment with a silane coupling agent, etc. or covered by a metal oxide film, etc.

[0054]

Though the thickness of the undercoat layer varies depending upon the blending composition of the undercoat layer, it can be arbitrarily set up within a range where adverse influences such as an increase of the residual potential are not detected, even when the photoreceptor is subjected to repeated continuous use. In general, the thickness of the undercoat layer is in the range from about 0.01 to 50 μ m. Furthermore, the undercoat layer may be a laminate.

[0055]

In the case where the photosensitive layer 3 is of a functionally separated type, it is mainly composed of two layers, including a charge generation layer 3a and a charge transport layer 3b, and in the case where the photosensitive layer 3 is of a single layer type, it is composed of a single layer. However, a laminate of plural layers having

the same kind of function may be employed.

[0056]

The charge generation layer 3a is formed by vacuum depositing an inorganic or organic photoconductive substance or formed by coating a material having a particles of an organic photoconductive substance dispersed in a resin binder, and has a function for receiving light to generate a charge. It is important that its efficiency of charge generation is high, and at the same time, injection properties of the generated charge into the charge transport layer 3b also are important. It is desired that the electric field dependency is low and that the injection is good even in a low electric field.

[0057]

Since the only required function of the charge generation layer is charge generation, its thickness is determined by a coefficient of light absorption of the charge generation substance and is usually in the range from 0.1 to 50 μm . In the case of a layered photoreceptor in which the charge transport layer is laminated on the charge generation layer, the thickness of the charge generation layer is generally not more than 5 μm , and suitably not more than 1 μm .

[0058]

The charge generation layer is composed mainly of a charge generation substance, to which can be added a charge transport substance, etc. Examples of the charge generation substance which can be used include phthalocyanine-based pigments, azo pigments, anthanthrone pigments, perylene pigments, perinone pigments, squarylium pigments, thiapyrylium pigments, and quinacridone pigments. Also, these pigments may be properly combined and used. In particular, a disazo pigment and a

trisazo pigment are suitable as the azo pigment;

N,N'-bis(3,5-dimethylphenyl)-3,4:9,10-perylenebis(carboxyimide) is suitable as the perylene pigment; and metal-free phthalocyanine, copper phthalocyanine, and titanyl phthalocyanine are suitable as the phthalocyanine-based pigment.

[0059]

In the invention, among these charge generation substances, phthalocyanine-based pigments are especially preferred for use. Such a phthalocyanine, includes a variety of crystal morphologies. In particular, X-type metal-free phthalocyanine, τ -type metal-free phthalocyanine, ϵ -type copper phthalocyanine, α -type titanyl phthalocyanine, β -type titanyl phthalocyanine, Y-type titanyl phthalocyanine, amorphous titanyl phthalocyanine, titanyl phthalocyanine having the maximum peak of 9.6° in terms of a Bragg angle 20 by a CuK α : X-ray diffraction spectrum as described in JP-A-08-209023, and the like, are known. Above all, for example, X-type metal-free phthalocyanine, α -type titanyl phthalocyanine, and Y-type titanyl phthalocyanine as described, for example, in JP-A-2001-228637, titanyl phthalocyanine according to the invention as described in JP-A-2001-330972, and the like are most preferred.

[0060]

Furthermore, among the foregoing charge generation substances, there are charge generation substances having a charge transport function in addition to the charge generation function. In particular, azo pigments and perylene pigments have electron transport properties and can also be used as an electron transport substance for other purposes than the purpose of generating a charge.

[0061]

As the resin binder for the charge generation layer, polyvinyl acetal resins, polyvinyl butyral resins, vinyl chloride resins, vinyl acetate resins, silicone resins, polycarbonate resins, polyester resins, polyethylene, polypropylene, polystyrene, acrylic resins, polyurethane resins, epoxy resins, melamine resins, polyamide resins, polystyrene resins, polyacetal resins, polyallylate resins, polysulfone resins, polymers or copolymers of methacrylic esters, and the like can be properly combined and used. A mixture of the same kind of resins having a different molecular weight may also be used. Incidentally, the resin binder is from 10 to 90 % by weight, and suitably from 20 to 80 % by weight of the charge generation layer.

[0062]

Here, in the case where a charge transport substance is added in the charge generation layer, it is possible to use a charge transport substance which is used in the charge transport layer as described later. Also, it is possible to use the compound represented by the foregoing general formula (I) according to the invention.

Incidentally, the charge transport substance to be added in the charge generation layer is from 0.1 to 50 % by weight of the charge generation layer.

[0063]

The charge transport layer 3b is a coating film comprising a material having a charge transport substance dispersed in a resin binder and functions to hold a charge of the photoreceptor as an insulator layer in a dark place and to transport a charge injected from the charge generation layer at the time of receiving light.

[0064]

The charge transport substance includes a hole transport substance and an electron transport substance. In the invention, it is at least required to use the compound represented by the foregoing general formula (I) as the electron transport substance. In the invention, it is also possible to use another electron transport substance or hole transport substance jointly in addition to such a compound. Incidentally, the content of the charge transport substance is from 10 to 90 % by weight, and preferably from 20 to 80 % by weight of the charge transport layer. When the compound represented by the foregoing general formula (I) according to the invention is contained in the charge transport layer, the effects of the invention are obtained. Its content is suitably from 10 to 60 % by weight, and more suitably from 15 to 50 % by weight of the charge transport layer.

[0065]

As other electron transport substances, heretofore known electron transport substances can be used in combination with the compound of the invention. Electron accepting substances and electron transport substances such as succinic anhydride, maleic anhydride, dibromosuccinic anhydride, phthalic anhydride, 3-nitrophthalic anhydride, 4-nitrophthalic anhydride, pyromellitic anhydride, pyromellitic acid, trimellitic acid, trimellitic acid, trimellitic anhydride, phthalimide, 4-nitrophthalimide, tetracyanoethylene, tetracyanodimethane, chloranil, bromanil, o-nitrobenzoic acid, trinitrofluorenone, quinone, benzoquinone, diphenoquinone, naphthoquinone, anthraquinone, and stilbenequinone can be used. In particular, compounds represented by the structural formulae (ET1-1) to (ET1-16), (ET2-1) to (ET2-16), (ET3-1) to (ET3-12), (ET4-1) to (ET4-32), (ET5-1) to (ET5-8), (ET6-1) to (ET6-50), (ET7-11) to (ET7-14), (ET8-1) to

(ET8-6), (ET9-1) to (ET9-4), (ET10-1) to (ET10-32), (ET11-1) to (ET11-16), (ET12-1) to (ET12-16), (ET13-1) to (ET13-16), (ET14-1) to (ET14-16), (ET15-1) to (ET15-16), (ET-1) to (ET-42), and the like as described in JP-A-2000-314969 are preferable. These electron accepting substances and electron transport substances can be used singly or in combinations of two or more thereof.

[0066]

Though the hole transport substance is not particularly limited, styryl compounds can be suitably used. Incidentally, the term "styryl compound" in this description means a compound having a structure represented by the following formula:

(in the foregoing formula, the hydrogen atoms may be substituted.)

[0067]

As the specific structure of the styryl compound, for example, there are enumerated compounds represented by the structural formulae (HT-1) to (HT1-136) and (HT2-1) to (HT2-70) as described in JP-A-2000-314969, the structural formulae (V-40) to (V-57) as described in JP-A-2000-204083, and the structural formulae (HT1-1) to (HT1-70) as described in JP-A-2000-314970, but it should not be construed that the invention is limited to these compounds.

[8900]

Other examples of the hole transport substance which can be used include hydrazone compounds, pyrazoline compounds, pyrazolone compounds, oxadiazole compounds, oxazole compounds, arylamine compounds, benzidine compounds,

stilbene compounds, polyvinylcarbazole, and polysilanes (with respect to specific structures thereof, for example, the structural formulae (HT3-1) to (HT3-39), (HT4-1) to (HT4-20), (HT5-1) to (HT5-10), and (HT-1) to (HT-37) as described in JP-A-2000-314969, which description is incorporated herein by reference). These hole transport substances can be used singly or in combinations of two or more thereof.

[0069]

As the resin binder for the charge transport layer, polycarbonate resins, polyester resins, polyvinyl acetal resins, polyvinyl butyral resins, vinyl chloride resins, vinyl acetate resins, polyethylene, polypropylene, polystyrene, acrylic resins, polyurethane resins, epoxy resins, melamine resins, phenol resins, silicon-based resins, silicone resins, polyamide resins, polystyrene resins, polyacetal resins, polyallylate resins, polysulfone resins, polymers or copolymers of methacrylic esters, and the like can be properly combined and used. In particular, there are enumerated polycarbonates having, as a principal repeating unit, a structural unit represented by any one of the structural formulae (BD1-1) to (BD1-16) as described in JP-A-2000-314969. Besides, polycarbonate resins and polyester resins having, as a principal repeating unit, one kind or two or more kinds of structural units represented by the structural formulae (BD-1) to (BD-7) as described in JP-A-2000-314969 are suitable, and these resins may be used in combination of two or more kinds thereof. Also, a mixture of the same kind of resins having a different molecular weight may be used. Incidentally, the content of the resin binder is from 10 to 90 % by weight, and preferably from 20 to 80 % by weight of the charge transport layer.

[0070]

In order to maintain a practically useful effective surface potential, the thickness of the charge transport layer is preferably in the range of from 3 to 100 μ m, and more preferably from 10 to 50 μ m.

[0071]

Incidentally, as the functionally separated layered photoreceptor, though a photoreceptor comprising a charge generation layer and a charge transport layer laminated thereon is generally used, a photoreceptor comprising a charge transport layer and a charge generation layer laminated thereon may be employed.

[0072]

In the case of a single layer type photosensitive layer, a charge generation substance, a charge transport substance, and a resin binder are used as the major components. The charge transport substance includes a hole transport substance and an electron transport substance. In the invention, it is at least required to use the compound represented by the foregoing general formula (I) as the electron transport substance. It is also possible to use other charge transport substances (electron transport substances and a hole transport substances) jointly as in the case of the foregoing charge transport layer 3b. It is desirable to use a hole transport substance jointly with the electron transport substance. With respect to the charge generation substance, the same compounds as in the charge generation substance which is used in the foregoing charge generation layer 3a can be used. Furthermore, with respect to the resin binder, the same materials as in the resin binder which is used in the foregoing charge transport layer 3b or the foregoing charge generation layer 3a can be used. Incidentally, the content of the charge generation substance is from 0.01 to 50 % by

weight, preferably from 0.1 to 20 % by weight, and more preferably from 0.5 to 10 % by weight of the single layer type photosensitive layer. Also, the content of the charge transport substance is from 10 to 90 % by weight, and preferably from 20 to 80 % by weight of the single layer type photosensitive layer. When the compound represented by the foregoing general formula (I) according to the invention is contained in the single layer type photosensitive layer, the effects of the invention are obtained. Its content is suitably from 10 to 60 % by weight, and preferably from 15 to 50 % by weight of the single layer type photosensitive layer. The content of the hole transport substance to be used jointly is suitably from 10 to 60 % by weight, and preferably from 20 to 50 % by weight of the single layer type photosensitive layer. The content of the resin binder is usually from 10 to 90 % by weight, and preferably from 20 to 80 % by weight of the single layer type photosensitive layer.

[0073]

In order to maintain a practically useful effective surface potential, the thickness of the single layer type photosensitive layer is preferably in the range of from 3 to 100 μ m, and more preferably from 10 to 50 μ m.

[0074]

For the purpose of enhancing the environmental resistance and the stability against light that causes deterioration of the photosensitive layer, it is possible to contain deterioration-preventing agents such as antioxidants and light stabilizers in such a photosensitive layer. Examples of compounds which are used for such a purpose include chromanol derivatives such as tocopherol, esterified compounds, polyarylalkane compounds, hydroquinone derivatives, etherified compounds, dietherified compounds.

benzophenone derivatives, benzotriazole derivatives, thioether compounds, phenylenediamine derivatives, phosphonic acid esters, phosphorous acid esters, phenol compounds, hindered phenol compounds, linear amine compounds, cyclic amine compounds, and hindered amine compounds.

[0075]

Furthermore, for the purposes of enhancing leveling properties of the formed film and imparting lubricating properties, it is possible to contain a leveling agent such as silicone oils and fluorine-based oils in the photosensitive layer.

[0076]

In addition, for the purposes of reducing a coefficient of friction and imparting lubricating properties or other purposes, fine particles of a metal oxide such as silicon oxide (silica), titanium oxide, zinc oxide, calcium oxide, aluminum oxide (alumina), and zirconium oxide, a metal sulfate such as barium sulfate and calcium sulfate, or a metal nitride such as silicon nitride and aluminum nitride, or fluorine-containing polymers or silicon-containing polymers such as particles of a fluorine-based resin such as a tetrafluoroethylene resin, fine particles of a silicone resin, and a fluorine-based comb-type graft polymerization resin may be contained in the photosensitive layer.

[0077]

In addition, it is also possible to contain other known additives within the range where the electrophotographic characteristics are not significantly impaired, as the need arises.

[0078]

The protective layer 4 can be provided, if desired for the purpose of enhancing

the printing resistance or other purposes. The protective layer 4 is made of one of the following: a layer containing a resin binder as the major component, an inorganic thin film as formed by film formation of amorphous carbon, amorphous silicon-carbon, etc. by vapor phase epitaxy, a coating film as formed by vapor deposition of silica, alumina, etc., or the like. As the resin binder, those as used in the foregoing charge transport layer 3b, three-dimensional crosslinked resins such as siloxane resins, and the like can be used. Furthermore, for the purposes of enhancing conductivity, reducing a coefficient of friction and imparting lubricating properties or other purposes, the resin binder may contain one of the following: fine particles of a metal oxide such as silicon oxide (silica), titanium oxide, zinc oxide, calcium oxide, aluminum oxide (alumina), or zirconium oxide, a metal sulfate such as barium sulfate or calcium sulfate, or a metal nitride such as silicon nitride or aluminum nitride, or fine particles of fluorine-containing polymers or silicon-containing polymers such as particles of a fluorine-based resin such as a tetrafluoroethylene resin, fine particles of a silicone resin, or a fluorine-based comb-type graft polymerization resin.

[0079]

Furthermore, for the purpose of imparting charge transport properties to the protective layer, it is possible for the protective layer to contain the foregoing charge transport substance, electron accepting substance and electron transport substance to be used in the photosensitive layer or the compound represented by the foregoing general formula (1); and for the purposes of enhancing leveling properties of the formed film and imparting lubricating properties, it is possible to contain a leveling agent such as silicone oils and fluorine-based oils.

[0080]

The only limitation on the thickness of the protective layer is that the functions of the photosensitive layer are not significantly impaired. In general, it is preferably in the range of from 0.1 to 50 μ m, and more preferably from 1 to 10 μ m. Also, the protective layer may be a laminate of plural layers.

[0081]

The method for preparing the photoreceptor of the invention will be hereunder described in detail (such a method being described in even more detail in *The Journal of Imaging Society of Japan*, Vol. 28, No. 2 (1989), pp.186-195, "Production technologies of OPC photoreceptors"). In the case where the foregoing undercoat layer 2, photosensitive layer 3 (charge generation layer 3a and charge transport layer 3b) and protective layer 4 are formed by coating, a method in which the foregoing constituent materials are dissolved and dispersed together with an appropriate solvent to prepare a coating liquid, which is then applied by an appropriate coating method, followed by drying to remove the solvent may be employed.

[0082]

Examples of such a solvent which is principally used include alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, and benzyl alcohol; ketones such as acetone, MEK (methyl ethyl ketone), methyl isobutyl ketone, and cyclohexanone; amides such as DMF (dimethylformamide) and dimethylacetamide; sulfoxides such as dimethyl sulfoxide; cyclic or linear ethers such as THF (tetrahydrofuran), dioxane, dioxolan, diethyl ether, methyl cellosolve, and ethyl cellosolve; esters such as methyl acetate, ethyl acetate, and n-butyl acetate; aliphatic halogenated hydrocarbons such as

methylene chloride, chloroform, carbon tetrachloride, dichloroethylene, and trichloroethylene; mineral oils such as ligroin; aromatic hydrocarbons such as benzene, toluene, and xylene; and aromatic halogenated hydrocarbons such as chlorobenzene and dichlorobenzne. These solvents may be used in admixture of two or more.

[0083]

As a method for dispersing and dissolving the foregoing coating liquid, known methods such as methods using a paint shaker (paint conditioner), a ball mill, or a bead mill such as a dyno mill (sand grinder), and ultrasonic dispersion can be employed. Furthermore, as a coating method, known methods such as a dip coating method, a ring coating method (seal coating), a spray coating method, a bar coating method, and a blade coating method can be employed.

[0084]

Moreover, though the temperature and drying time in the foregoing drying process can be properly set while taking into consideration the type of solvent to be used, the production costs, and so on, it is preferable that the drying temperature is set within the range of from room temperature to 200°C and that the drying time is set in the range of from 10 minutes to 2 hours. It is more preferable that the drying temperature fall between the boiling point of the solvent and 80°C above the boiling point. Also, this drying is usually carried out in a stationary state or while air is being blown at or under atmospheric pressure.

[0085]

The electrophotographic photoreceptor of the invention can be used in known electrophotographic processes; can be suitably used in a general electrophotographic

process including charge, exposure, development, transfer and fixation; and can be used in copiers, printers, facsimiles, etc. that apply such an electrophotographic process.

[0086]

Here, the charge process includes a positive charge process for positively charging a photoreceptor and a negative charge process for negatively charging a photoreceptor. Though the photoreceptor of the invention can be used in the negative charge process, it is preferably used in the positive charge process because it exhibits especially high sensitivity in the positive charge process. In particular, an electrophotographic photoreceptor in which the photosensitive layer is a single layer type photosensitive layer containing a charge generation substance, a charge transport substance, and a resin binder; an electron transport substance and a hole transport substance are contained as the charge transport substance; and at least one compound represented by the foregoing general formula (I) according to the invention is contained as the electron transport substance, has high sensitivity in the positive charge process.

[0087]

A charger in the charge process includes a non-contact charger using a corotron or a scorotron and a charger in a roll form or brush form for performing a charge in contact with, or in close vicinity to a photoreceptor. The photoreceptor of the invention can be used in a process using any of these chargers.

[8800]

In the exposure process, light sources having a wavelength region to which the photoreceptor is sensitive are usually used, and white light emitted from a halogen lamp,

a fluorescent lamp, etc., laser light, LED (light emitting diode) light, and the like are suitable. In particular, in the case where phthalocyanine is used as the charge generation substance, semiconductor laser light in the vicinity of from 600 to 800 nm and LED light are most suitable. Also, by using a transparent material as an electrically conductive substrate of the photoreceptor, an internal exposure system can be employed.

[0089]

The development process should preferably include a dry development system using a dry toner or a liquid development (wet development) system using a liquid toner. The photoreceptor of the invention can be used in either of these systems. Incidentally, in the case of a liquid development system, it is desired to take known measures such that the components of the photoreceptor do not wash out in the solvent which is contained in the liquid toner.

[0090]

Furthermore, the development process includes a reverse development system for developing a toner in an exposed area and a normal development system for developing a toner in a non-exposed area. In particular, in the case of using phthalocyanine as the charge generation substance, it is preferable that the photoreceptor is used in a process of the reverse development system.

[0091]

A known electrophotographic process includes cleaning after a transfer process, for the purpose of removing or scattering any untransferred toner remaining in the photoreceptor. Known electrophotographic processes also may exclude such a

FEC 165NP

cleaning process. The photoreceptor of the invention can be used in both processes.

[0092]

Furthermore, known electrophotographic processes may or may not include a destaticization process that is performed by exposure after a transfer process for the purpose of removing a charge remaining in the photoreceptor or standardizing the surface potential. The photoreceptor of the invention can be used in both processes.

[0093]

Moreover, the electrophotographic apparatus of the invention is characterized by being provided with the foregoing electrophotographic photoreceptor of the invention and performing a positive charge process. The electrophotographic apparatus of the invention is not particularly limited with respect to the charge process and may be constructed by the general process described previously.

EXAMPLES

[0094]

The invention will be hereunder described with reference to the Examples.

Synthesis Example 1: Synthesis of compound of the foregoing specific example (I-3)

A compound represented by the foregoing specific example (I-3) was synthesized according to the following reaction schemes (1-1) and (2-1).

Reaction scheme (1-1)

Reaction scheme (2-1)

[0095]

(1) To a dichloromethane solution of 100 mmoles (14.7 g) of 2-thenoyl chloride (the foregoing structural formula (B'-1)) and 110 mmoles (10.7 g) of N,O-dimethylhydroxyamine hydrochloride, 230 mmoles (18.2 g) of pyridine was added at room temperature in a nitrogen atmosphere, and the mixture was stirred for 2 hours. Thereafter, the reaction liquid was poured into aqueous hydrochloric acid and extracted with dichloromethane, followed by concentration. There was thus obtained, as a crude product, N-methoxy-N-methylthiophenecarboxamide (the foregoing structural formula (B-1)) in a yield of 14.8 g (86.7 %).

[0096]

(2) Next, to a tetrahydrofuran (THF) solution of 30 mmoles (5.1 g) of the compound represented by the foregoing structural formula (B-1), a Grignard reagent as prepared from 78 mmoles (1.9 g) of magnesium and a THF solution of 60 mmoles (21.4 g) of 4-bromo-2,6-di-t-butyl-1-(trimethylsiloxy)benzene (A-1) was added dropwise, and the

mixture was stirred at room temperature for 3 hours. Thereafter, a small amount of a 1N hydrochloric acid aqueous solution was added to stop the reaction. In addition, 60 mmoles (60 mL) of a THF solution of 1.0 M tetrabutylammonium fluoride (TBAF) was added, followed by stirring. The reaction liquid was poured into aqueous hydrochloric acid and extracted with dichloromethane, followed by concentration. There was thus obtained, as a crude product, a compound represented by the structural formula (C-1) in a yield of 6.5 g (68.1 %).

[0097]

(3) In addition, 15 mmoles (4.7 g) of the compound represented by the foregoing structural formula (C-1) and 30 mmoles (5.4 g) of 4-chlorophenylhydrazine hydrochloride (the foregoing structural formula (D-1)) were dissolved in pyridine, and the mixture was refluxed under heat. The reaction liquid was poured into aqueous hydrochloric acid and extracted with dichloromethane, followed by concentration. Thereafter, the resulting product was purified by column chromatography to obtain a crude product.

[0098]

(4) To a chloroform solution of the foregoing crude product, 20 mmoles (4.8 g) of lead dioxide (PbO₂) was added at room temperature, and the mixture was stirred. After the residue was filtered out, the reaction liquid was concentrated, and the resulting solid was recrystallized from hexane to obtain a compound represented by the foregoing structural formula (I-3). Yield: 3.4 g (percent yield: 51.4 %), MS: m/z 438 (M+). Incidentally, the entire yield was 30.3 %. The IR spectrum and ¹H-NMR spectrum of this compound of the specific example (I-3) are shown in Fig. 7 and Fig. 8, respectively.

[0099]

Synthesis Example 2: Synthesis of compound of the foregoing specific example (I-83)

A compound represented by the foregoing specific example (I-83) was synthesized according to the following reaction schemes (1-2) and (2-2).

Reaction scheme (1-2)

Reaction scheme (2-2)

TMSO Br i) Mg TMSO TBAF HO (C-2)

$$(A-1) \qquad (B-2) \qquad (C-2)$$

$$H_2N-NH- CI \qquad (D-1) \qquad HO \qquad (I-83)$$

$$[0100]$$

As shown in the foregoing reaction schemes, a compound represented by the foregoing structural formula (I-83) was obtained by following the same operations as in Synthesis Example 1, except for changing the 2-thenoyl chloride (the foregoing structural formula (B'-1)) in the foregoing Synthesis Example 1 to 2-furoyl chloride (the foregoing structural formula (B'-2)). Yield: 3.1 g (entire yield: 32.5 %), MS: m/z 422 (M+). The IR spectrum and ¹H-NMR spectrum of this compound of the specific

example (I-83) are shown in Fig. 9 and Fig. 10, respectively.

[0101]

Synthesis Example 3: Synthesis of compound of the foregoing specific example (I-163)

A compound represented by the foregoing specific example (I-163) was synthesized according to the following reaction schemes (1-3) and (2-3).

Reaction scheme (1-3)

Reaction scheme (2-3)

[0102]

As shown in the foregoing reaction schemes, a compound represented by the foregoing structural formula (I-163) was obtained by following the same operations as in Synthesis Example 1, except for changing the 2-thenoyl chloride (the foregoing structural formula (B'-1)) in the foregoing Synthesis Example 1 to

benzo[b]thiophene-2-carboxylic acid chloride (the foregoing structural formula (B'-3)). Yield: 5.0 g (entire yield: 41.2 %), MS: m/z 488 (M+). The IR spectrum and ¹H-NMR spectrum of this compound of the specific example (I-163) are shown in Fig. 11 and Fig. 12, respectively.

[0103]

Synthesis Example 4: Synthesis of compound of the foregoing specific example (I-217)

A compound represented by the foregoing specific example (I-217) was synthesized according to the following reaction schemes (1-4) and (2-4).

Reaction scheme (1-4)

Reaction scheme (2-4)

[0104]

As shown in the foregoing reaction schemes, a compound represented by the

foregoing structural formula (I-217) was obtained by following the same operations as in Synthesis Example 1, except for changing the 2-thenoyl chloride (the foregoing structural formula (B'-1)) in the foregoing Synthesis Example 1 to 3-chlorobenzo[b]thiophene-2-carboxylic acid chloride (the foregoing structural formula (B'-4)). Yield: 4.6 g (entire yield: 26.3 %), MS: m/z 522 (M+). The IR spectrum and ¹H-NMR spectrum of this compound of the specific example (I-217) are shown in Fig. 13 and Fig. 14, respectively.

[0105]

Synthesis Example 5: Synthesis of compound of the foregoing specific example (I-243)

A compound represented by the foregoing specific example (I-243) was synthesized according to the following reaction schemes (1-5) and (2-5).

Reaction scheme (1-5)

Reaction scheme (2-5)

[0106]

As shown in the foregoing reaction schemes, a compound represented by the foregoing structural formula (I-243) was obtained by following the same operations as in Synthesis Example 1, except for changing the 2-thenoyl chloride (the foregoing structural formula (B'-1)) in the foregoing Synthesis Example 1 to benzo[b]furan-2-carboxylic acid chloride (the foregoing structural formula (B'-5)). Yield: 4.8 g (entire yield: 32.8 %), MS: m/z 472 (M+). The IR spectrum and ¹H-NMR spectrum of this compound of the specific example (I-243) are shown in Fig. 15 and Fig. 16, respectively.

[0107]

Synthesis Example 6: Synthesis of compound of the foregoing specific example (I-403)

A compound represented by the foregoing specific example (I-403) was synthesized according to the following reaction schemes (1-6) and (2-6).

Reaction scheme (1-6)

Reaction scheme (2-6)

[0108]

As shown in the foregoing reaction schemes, a compound represented by the foregoing structural formula (I-403) was obtained by following the same operations as in Synthesis Example 1, except for changing the 2-thenoyl chloride (the foregoing structural formula (B'-1)) in the foregoing Synthesis Example 1 to 3,4-ethylenedioxythiophene-2-carboxylic acid chloride (the foregoing structural formula (B'-6)). Yield: 2.8 g (entire yield: 38.9 %), MS: m/z 496 (M+). The IR spectrum and ¹H-NMR spectrum of this compound of the specific example (I-403) are shown in Fig. 17 and Fig. 18, respectively.

[0109]

Incidentally, the 2-thenoyl chloride (the foregoing structural formula (B'-1)), the

2-furoyl chloride (the foregoing structural formula (B'-2)) and the 4-chlorophenylhydrazine hydrochloride (the foregoing structural formula (D-1)) are available from Tokyo Kasei Kogyo Co., Ltd. and the like. Furthermore, the benzo[b]thiophene-2-carboxylic acid chloride (the foregoing structural formula (B'-3)) and the 3-chlorobenzo[b]thiophene-2-carboxylic acid chloride (the foregoing structural formula (B'-4)) are available from Lancaster Japan K.K. and the like. In addition, the 4-bromo-2,6-di-tert-butyl-1-(trimethylsiloxy)benzene (the foregoing structural formula (A-1)) can be, for example, synthesized by a known method as described in the foregoing Patent Document 14 and so on.

[0110]

Furthermore, the benzo[b]furan-2-carboxylic acid chloride (the foregoing structural formula (B'-5)) was synthesized according to the following reaction scheme (3).

Reaction scheme (3)

[0111]

To 50 mmoles (8.1 g) of benzo[b]furan-2-carboxylic acid, 75 mmoles (8.9 g) of thionyl chloride was added, and three drops of N,N-dimethylformamide was added dropwise, followed by refluxing under heat for 2 hours. The excess thionyl chloride was evaporated off to obtain, as an oily substance, benzo[b]furan-2-carboxylic acid chloride (the foregoing structural formula (B'-5)) in a yield of 7.4 g (81.9 %).

Incidentally, the benzo[b]furan-2-carboxylic acid is available from Sigma-Aldrich Japan K.K. and the like.

[0112]

In addition, 3,4-ethylenedioxythiophene-2-carboxylic acid chloride (the foregoing structural formula (B'-6)) was synthesized according to the following reaction scheme (4).

Reaction scheme (4)

[0113]

(1) To a hexane solution of 200 mmoles (28.4 g) of 3,4-ethylenedioxythiophene and 220 mmoles (25.6 g) of N,N,N,N-tetramethylenediamine, 220 mmoles (138 mL) of n-BuLi was added dropwise in an ice bath in a nitrogen atmosphere. Thereafter, the mixture was agitated at room temperature for 0.5 hours and additionally refluxed under heat for 0.5 hours. The reaction liquid was cooled and then poured into dry ice, followed by allowing it to stand overnight. Thereafter, the reaction liquid was extracted in two serial extraction steps respectively with chloroform and a 10 % sodium hydroxide aqueous solution. When the resulting aqueous solution was made acidic with hydrochloric acid, a precipitate was deposited. By performing filtration, 3,4-ethylenedioxythiophene-2-carboxylic acid was obtained as a crude product in a yield of 21.8 g (percent yield: 58.5 %).

[0114]

(2) To 50 mmoles (9.3 g) of the resulting 3,4-ethylenedioxythiophene-2-carboxylic acid, 75 mmoles (8.9 g) of thionyl chloride was added, and three drops of N,N-dimethylformamide was added dropwise, followed by refluxing under heat for 2 hours. The excess thionyl chloride was evaporated off to obtain, as an oily substance, 3,4-ethylenedioxythiophene-2-carboxylic acid chloride (the foregoing structural formula (B'-6)) in a yield of 7.9 g (77.2 %).

Incidentally, the 3,4-ethylenedioxythiophene is available from Sigma-Aldrich Japan K.K. and the like.

[0115]

Photoreceptor Example 1

A plate-like photoreceptor for evaluating electrical characteristics and a drum-like photoreceptor for evaluating printing were prepared, respectively. Incidentally, the term "parts," whenever its meaning is unspecified, means parts by weight.

A solution for the undercoat layer as prepared in the following manner was coated on the external surface of each of an aluminum plate (3 cm \times 10 cm, thickness: 1 mm) and an aluminum drum (outer diameter: 30 mm ϕ , length: 247.5 mm, thickness: 0.75 mm) by the dip coating method and then dried at 100°C for 60 minutes to remove the solvent. There was thus formed an undercoat layer having a thickness of 0.3 μ m.

[0116]

(Preparation of solution for undercoat layer)

• a1) Soluble nylon (AMILAN CM8000, manufactured by Toray Industries, Inc.): 3 parts by weight (30 g)

The foregoing material a1) for the undercoat layer was stirred together with 97 parts by weight (970 g) of a mixed solvent of methanol/methylene chloride (5 vol./5 vol.) and dissolved to prepare a solution for the undercoat layer.

[0117]

Next, on this undercoat layer, a dispersion for single layer type photosensitive layer as prepared in the following manner was coated by the dip coating method for the plate-like photoreceptor and by the ring coating method for the drum-like photoreceptor, respectively and then dried at 100° C for 60 minutes to remove the solvent. Thus, a single layer type photosensitive layer having a thickness of 30 μ m was formed, from which was then prepared an electrophotographic photoreceptor.

[0118]

(Preparation of dispersion for single layer type photosensitive layer)

- b1) Charge generation substance: X-type metal-free phthalocyanine (see Fig. 2 of JP-A-2001-228637): 0.2 parts by weight (0.1 g)
- b2) Hole transport substance: Styryl compound represented by the following structural formula (HT1-101) ((HT1-101) of JP-A-2000-314969): 8 parts by weight (4 g)

- b3) Electron transport substance: Compound represented by the foregoing formula (I-3) [Synthesis Example 1]: 5 parts by weight (2.5 g)
- b4) Antioxidant: 3,5-di-tert-4-hydroxytoluene (BHT): 1 part by weight (0.5 g)

- b5) Silicone oil (KF-50: manufactured by Shin-Etsu Chemical Co., Ltd.): 0.01 parts by weight (0.005 g)
- b6) Binder resin: Bisphenol Z-type polycarbonate resin (PANLITE TS2050, manufactured by Teijin Chemicals Ltd.) ((BD1-1) of JP-A-2000-314969): 7 parts by weight (3.5 g)

[0119]

In a 100-mL plastic bottle, the foregoing materials b1) to b6) for the photosensitive layer were charged together with 100 parts by weight (50 g) of a methylene chloride solvent and 50 g of stainless steel beads (3 mmφ), and the mixture was subjected to a dispersing treatment for 60 minutes by a paint conditioner Model 5400 (Red Devil Equipment Co., U.S.A.). Thereafter, the stainless steel beads were separated to prepare a dispersion for a single layer type photosensitive layer.

[0120]

Photoreceptor Example 2

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 5 parts by weight of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts by weight of the compound represented by the foregoing formula (I-83) [Synthesis Example 2].

[0121]

Photoreceptor Example 3

A photoreceptor was prepared in the same manner as in Photoreceptor

Example 1, except that in the composition of the dispersion for single layer type photosensitive layer as used in Photoreceptor Example 1, the amount of the styryl compound represented by the foregoing formula (HT1-101) was changed from 8 parts to 7 parts by weight; that the amount of the compound represented by foregoing formula (I-3) as an electron transport substance was changed from 5 parts to 2 parts; and that the amount of the bisphenol Z-type polycarbonate resin was changed from 7 parts to 10 parts.

[0122]

Photoreceptor Example 4

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 8 parts by weight of the styryl compound represented by the foregoing formula (HT1-101) as the hole transport substance was replaced by 8 parts by weight of a styryl compound represented by the following structural formula (HT2-2) ((HT2-2) of JP-A-2000-314969).

$$H_3C$$
 N
 $CH=C$
 H_2C
 $(H T 2 - 2)$

[0123]

Photoreceptor Example 5

A photoreceptor was prepared in the same manner as in Photoreceptor

Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 8 parts by weight of the styryl compound represented by the foregoing formula (HT1-101) as the hole transport substance was replaced by 8 parts by weight of a diamine compound represented by the following structural formula (HT-11) ((HT-11) of JP-A-2000-314969).

$$\begin{array}{c}
H_3C \\
N - N - N \\
CH_2
\end{array}$$
(H T - 1 1)

[0124]

Photoreceptor Example 6

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, the amount of the X-type metal-free phthalocyanine as the charge generation substance was changed from 0.2 parts to 0.3 parts.

[0125]

Photoreceptor Example 7

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 0.2 parts of the X-type metal-free phthalocyanine as the charge generation substance was replaced by 0.3 parts of α -type titanyl phthalocyanine (see Fig. 3 of JP-A-2001-228637).

[0126]

Photoreceptor Example 8

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 0.2 parts of the X-type metal-free phthalocyanine as the charge generation substance was replaced by 0.1 parts of Y-type titanyl phthalocyanine (see Fig. 4 of JP-A-2001-228637).

[0127]

Photoreceptor Example 9

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 0.2 parts of the X-type metal-free phthalocyanine as the charge generation substance was replaced by 0.1 parts of amorphous titanyl phthalocyanine (see Fig. 5 of JP-A-2001-228637).

[0128]

Photoreceptor Example 10

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 0.2 parts of the X-type metal-free phthalocyanine as the charge generation substance was replaced by 0.2 parts of a bisazo compound represented by the following structural formula (CG1-1).

[0129]

Photoreceptor Example 11

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that to the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 0.2 parts of a bisazo compound represented by the foregoing structural formula (CG1-1) was further added as an electron transport substance.

[0130]

Photoreceptor Example 12

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a compound represented by the foregoing formula (I-163) [Synthesis Example 3] as an electron transport substance.

[0131]

Photoreceptor Example 13

A photoreceptor was prepared in the same manner as in Photoreceptor

Example 1, except that in the composition of the dispersion for a single layer type

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photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a compound represented by the foregoing formula (I-217) [Synthesis Example 4] as an electron transport substance.

[0132]

Photoreceptor Example 14

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a compound represented by the foregoing formula (I-243) [Synthesis Example 5] as an electron transport substance.

[0133]

Photoreceptor Example 15

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a compound represented by the foregoing formula (I-403) [Synthesis Example 6] as an electron transport substance.

[0134]

Photoreceptor Comparative Example 1

A photoreceptor was prepared in the same manner as in Photoreceptor

Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a stilbenequinone compound represented by the following structural formula (ET-1) (manufactured by Tokyo Kasei Co., Ltd.).

[0135]

Photoreceptor Comparative Example 2

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a diphenoquinone compound represented by the following structural formula (ET-2).

[0136]

Photoreceptor Comparative Example 3

A photoreceptor was prepared in the same manner as in Photoreceptor

Example 1, except that in the composition of the dispersion for a single layer type

photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a compound represented by the following structural formula (ET-3).

$$O = CH-N=N-C$$
(E T - 3)

[0137]

Photoreceptor Comparative Example 4

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a compound represented by the following structural formula (ET-4).

$$O = C - N = N - Cl$$

$$CH_3$$
(E T - 4)

[0138]

Photoreceptor Comparative Example 5

A photoreceptor was prepared in the same manner as in Photoreceptor

Example 1, except that in the composition of the dispersion for a single layer type

photosensitive layer as used in Photoreceptor Example 1, 5 parts of the compound

represented by the foregoing formula (I-3) as the electron transport substance was replaced by 5 parts of a compound represented by the following structural formula (ET-5).

$$O = C - N = N - CI \qquad (E T - 5)$$

[0139]

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Photoreceptor Comparative Example 6

A photoreceptor was prepared in the same manner as in Photoreceptor Example 1, except that in the composition of the dispersion for a single layer type photosensitive layer as used in Photoreceptor Example 1, the compound represented by the foregoing formula (I-3) as the electron transport substance was not contained.

[0140]

Evaluation of Photoreceptor Examples 1 to 15 and Photoreceptor Comparative Examples 1 to 6

Using a plate-like photoreceptor for evaluating electrical characteristics, the evaluation was carried out by an electrostatic copying paper analyzer EPA-8100 as manufactured by Kawaguchi Electric Works Co., Ltd.

The photoreceptor was charged in a dark place in an atmosphere at a temperature of 24°C and a humidity of 50 % such that the surface potential became about +700 V, and a retention rate V_{k5} of the surface potential after a lapse of 5 seconds was determined according to the following expression.

Retention rate V_{k5} (%) = $(V_5/V_0) \times 100$

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V₀: Surface potential immediately after charging

V₅: Surface potential 5 seconds after charging

[0141]

[0142]

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Next, the surface potential was changed to +600 V, monochromic light of 1.0 μ V/cm² resulting from separation of light of a halogen lamp into 780 nm (but into 550 nm with respect to the Photoreceptor Example 10) was exposed for 5 seconds, the amount of exposure required until the surface potential became one-half (+300 V) was determined as a sensitivity $E_{1/2}$ (μ J/cm²), and the surface potential 5 seconds after the exposure was determined as a residual potential V_r (V).

Furthermore, the appearance of the prepared drum-like photoreceptor was visually observed.

The results of these evaluations are shown in the following Table 1.

Table 1

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	Retention rate V _{k5} (%)	Sensitivity E _{1/2} (μJ/cm²)	Residual potential V _r (V)	Appearance of photoreceptor
Photoreceptor Example 1	84.7	0.22	34	Good
Photoreceptor Example 2	79.8	0.32	45	Good
Photoreceptor Example 3	85.9	0.34	49	Good
Photoreceptor Example 4	80.6	0.28	46	Good
Photoreceptor Example 5	78.9	0.31	55	Good
Photoreceptor Example 6	82.0	0.19	30	Good
Photoreceptor Example 7	81.0	0.15	28	Good
Photoreceptor Example 8	83.3	0.20	31	Good
Photoreceptor Example 9	82.1	0.21	37	Good
Photoreceptor Example 10 *)	86.7	0.38	53	Good
Photoreceptor Example 11	79.5	0.19	29	Good
Photoreceptor Example 12	85.5	0.20	29	Good
Photoreceptor Example 13	84.3	0.19	26	Good
Photoreceptor Example 14	82.3	0.29	39	Good
Photoreceptor Example 15	84.6	0.23	36	Good
Photoreceptor Comparative Example 1	71.3	0.57	89	Deposited
Photoreceptor Comparative Example 2	69.7	0.65	98	Deposited
Photoreceptor Comparative Example 3	84.2	0.38	55	Good
Photoreceptor Comparative Example 4	81.5	0.35	53	Good
Photoreceptor Comparative Example 5	82.8	0.34	50	Slightly deposited
Photoreceptor Comparative Example 6	80.5	0.50	105	Good

^{*)} Exposure light: 550 nm

[0143]

Though the retention rate, sensitivity and residual potential of the photoreceptors of Photoreceptor Comparative Example 3 and Photoreceptor Comparative Example 4 were relatively good, they were slightly worse as compared with those of the photoreceptor of Photoreceptor Example 1 as prepared in the same

manner except for the electron transport substance.

[0144]

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Furthermore, for evaluating the durability by actual printing, each drum-like photoreceptor was installed in a laser printer HL-1850 as manufactured by Brother Industries, Ltd. and printed with a black solid image, a white solid image, and a half-tone image, respectively in an atmosphere at a temperature of 25°C and a humidity of 48 %. Subsequently, 5,000 sheets were printed with an image having a rate of printing of about 5 %. Thereafter, a black solid image, a white solid image, and a half-tone image were again printed, respectively, thereby evaluating the image after printing 5,000 sheets.

[0145]

As a result, in the photoreceptors of Photoreceptor Examples 1 to 6, 8, 9 and 11 to 15 and Photoreceptor Comparative Examples 3 and 4, a good image was obtained in both the initial image and the image after printing 5,000 sheets. On the other hand, in the photoreceptors of Photoreceptor Comparative Examples 1, 2 and 5, image unevenness which is seemed to be caused by deposition was generated in the initial half-tone image. In the photoreceptor of Photoreceptor Comparative Example 6, the image density was insufficient in the initial black solid image and the half-tone image. Incidentally, the photoreceptor of Photoreceptor Example 10 did not have sufficient sensitivity in a laser wavelength region (in the vicinity of 780 nm) of the used laser printer and therefore, it was noted that this photoreceptor is not suitable for this laser printer. Furthermore, in the photoreceptor of Photoreceptor Example 7, the sensitivity was too high so that this photoreceptor is less appropriate for this laser printer, and the

half-tone image was slightly broken.

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